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CONFORMATIONAL POLYMORPHISM OF NI(NCS)2 (P(CH2CH2CN)3)2: A CRYS--ETC(U)
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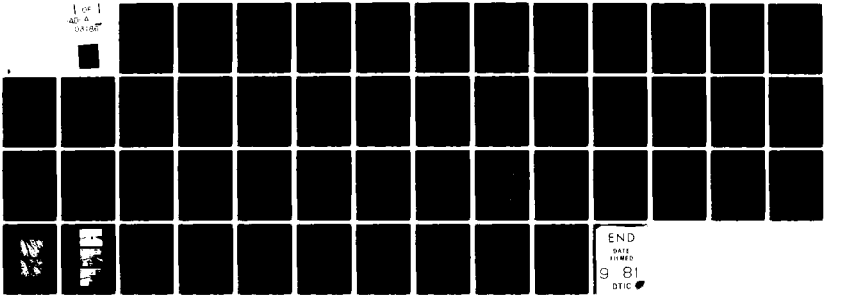

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Three conformational polymorphs of $Ni[NCS]_2[P(CH_2CH_2CN)_3]_2$ have been synthesized and their crystal structures determined by single-crystal X-ray diffraction techniques. All three crystallize in space group $P2_1/c$: cell constants for polymorph 1, a = 13.44(2) Å, b = 9.04(1) Å, c = 24.45 (2) Å, and β = 115.4(1)°; polymorph 2, a = 16.153 (5) Å, b = 12.393 (4) Å, c= 13.852 (4) Å and β = 107.89 (4)°; polymorph 3, a = 11.032(3) Å, b = 10.335 (3) Å, c = 11.801(4 Å and β = 107.21(5)°. Full matrix least-squares

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refinement of positional and thermal parameters led to R = 0.205, R_w = 0.224; R = 0.070, R_w = 0.107; and R = 0.038, R_w = 0.045 for polymorphs 1, 2, and 3, respectively, with 519, 2499 and 1852 reflections ($F > 3.9\sigma(F)$).

All three complexes have the expected square-planar geometry. However, polymorphs 2 and 3 have distinct bonding and packing environments, while the packing and non-bonded interactions of polymorph 1 display features common to both.

The crystal structures may be viewed as a closed set in terms of possible packing modes. Polymorph 2 has two intramolecular nonbonded nitrile N-Ni contacts (3.17 and 3.18 Å) occupying "pseudo-octahedral" positions. Polymorph 3 has two intermolecular nonbonded isothiocyanante S atom contacts (3.48 Å) in "pseudo-octahedral" positions. Polymorph 1 has both distinct features trans to one another. The crystal structure of polymorph 1 is composed of molecules interacting along two "noncross-linked" helical arrangements; polymorph 3 is composed of molecules interacting along cross-linked helical arrangements. However, the three polymorphs are not physically interconvertible. Polymorph 3 undergoes a reversible phase change at 78°C to a fourth polymorphic form.

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The Conformational Polymorphism of $Ni(NCS)_2[P(CH_2CH_2CN)_3]_2$: A Crystallographic Study of Three Polymorphs

by

Bruce M. Foxman and Harry Mazurek

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The Conformational Polymorphism of $Ni(NCS)_2[P(CH_2CH_2CN)_3]_2$: A Crystallographic Study of Three Polymorphs

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Contribution from the Department of Chemistry
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Abstract: Three conformational polymorphs of $Ni[NCS]_2[P(CH_2CH_2CN)_3]_2$ have been synthesized and their crystal structures determined by single-crystal X-ray diffraction techniques. All three crystallize in space group $P2_1/c$: cell constants for polymorph 1, a = 13.44(2) Å, b = 9.04(1) Å, c = 24.45(2) Å, and β = 115.4(1)°; polymorph 2, a = 16.153(5) Å, b = 12.393(4) Å, c = 13.852(4) Å, and β = 107.89(4)°; polymorph 3, a = 11.032(3) Å, b = 10.335(3) Å, c = 11.801(4) Å, and β = 107.21(5)°. Full matrix least-squares refinement of positional and thermal parameters led to R = 0.205, R_w = 0.224; R = 0.070, R_w = 0.107; and R = 0.038, R_w = 0.045 for polymorphs 1, 2, and 3, respectively, with 519, 2499 and 1852 reflections ($F > 3.92\,\sigma(F)$).

All three complexes have the expected square-planar geometry. However, polymorphs 2 and 3 have distinct bonding and packing environments, while the packing and non-bonded interactions of polymorph 1 display features common to both.

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Introduction

Square-planar complexes of the type NiX_2CEP_2 (X = Cl, Br, or I; CEP = $P(CH_2CH_2CN)_3$) undergo a series of interesting solid-state transformations. Thus the square-planar, monomeric chloro- and bromo- complexes react in the solid state to form an octahedral polymer, where the nickel centers are bridged by -P-CH_2-CH_2-C≡N- moieties.[1-3] These single-crystal reactions are characterized by crystallographic and chemical specificity, as well as high stereodirectionality.

The present study of the NiX_2CEP_2(X = NCS) system was prompted by several exemplary observations:

(i) for X = NCS, polymerization does not occur, presumably owing to the increased stability of the square planar monomers with isothiocyanato ligands, but it is nevertheless of interest to compare the structures of these complexes with those where X = Cl, Br or I; (ii) solid state reactions may be viewed as pure polymorphic transitions. Since polymerization occurs for X = Cl and Br, but not for X = NCS (vide infra) the observation of possible phase transitions in the absence of a chemical reaction is of interest; and (iii) the role of the polyfunctional ligand CEP in promoting polymorphism or polymorphic transitions could be examined.

Syntheses of the square-planar $Ni(NCS)_2CEP_2$ complex lead to the formation of three room-temperature polymorphs and, occasionally, a bis(β-hydroxy ketone)chelate complex, [Ni(diacetone alcohol)$_2$] [$Ni(NCS)_4CEP_2$].[4] One of the polymorphs transforms reversibly at 78°C to form a unique fourth polymorph. This paper reports the results of an X-ray structural study on the configurational and packing interrelationships among the various polymorphs.

Experimental Section

General. X-ray powder and Gandolfi patterns were obtained using a Supper powder/Gandolfi camera. The powder pattern of the high temperature polymorph (vide infra) was obtained using a black paper sleeve for the film and heating the capillary in the "open" camera with a Blake Industries Single Crystal Heater set between 80°C and 100°C.

Synthesis of polymorph 1. $Ni(NCS)_2$ (1.0 g, 5.7 mmol, ROC/RIC), CEP (2.2 g, 11.5 mmol, Aldrich), 10 ml of reagent grade acetone, and 10 ml of absolute ethanol were mixed, and unreacted material removed by filtration. The red-orange flocculent product formed in the filtrate, and was dried for 20 hrs in a vacuum desiccator at room temperature.

Anal. Calcd. for $Ni(CEP)_2(NCS)_2$: C 42.80; H 4.31; N 19.96. Found: C 42.95; H, 4.62; N 19.85: (Galbraith Laboratories, Inc.) Single, needle-shaped crystals were grown by dissolving $Ni(NCS)_2$ (0.10 g, 0.57 mmol) and CEP (0.11 g, 0.57 mmol) in 30 ml of CH_3CN. This was poured into one arm of an U-tube divided by a sintered glass disc; absolute ethanol (30 ml) was poured into the other arm. Poor quality single crystals were obtained by slow diffusion over a two month period. X-ray powder diffraction showed these crystals to be identical to the flocculent material.

Synthesis of polymorph 2. $Ni(NCS)_2$ (1.0 g, 5.7 mmol), CEP (2.2 g, 11.5 mmol), 10 ml of reagent grade acetone, 12 ml of absolute ethanol, and 2 ml of triethyl orthoformate were mixed in a stoppered flask. After two days a red product crystal was picked from among the flocculent precipitate. To date only one crystal of this form has been found!

Synthesis of polymorph 3. Nearly all crystals found on the flocculent precipitate (see Synthesis of polymorph 2) are of the

third form. However, a procedure has been developed to grow large crystals of these relatively free of the flocculent precipitate. $Ni(NCS)_2$ (0.10 g, 0.57 mmol), CEP (0.11 g, 0.57 mmol), and 10 ml of distilled 4-hydroxy-4-methyl-2-pentanone (diacetone alcohol) were mixed and filtered. The filtrate was collected in a test tube; 10 ml of absolute ethanol was added. The test tube was loosely covered and allowed to stand for five days, during which the red product crystals formed.

Synthesis of high temperature polymorph 4. Crystals of polymorph 3 react at 78° to form an orange-red phase which reverts to polymorph 3 upon cooling below the transition temperature.

Collection and Reduction of Diffraction Data. Preliminary Weissenberg and precession photographs exhibited systematic absences ($h0\ell$, ℓ odd; $0k0$, k odd) and symmetry indicative of the space group $P2_1/c$ for all three polymorphs. Laué photographs were taken of each polymorph to determine crystal quality, and the respective crystals were transferred to a Supper No. 455 goniometer and optically centered on a Syntex $P2_1$ diffractometer. Most operations were performed as described previously;[4,5] other operations are described below. Details of the structure analyses, in outline form, are presented in Table I.

Solution and Refinement of the Structures: General. Initial computational work on polymorph 2 was performed on the University PDP-10 computer, using local versions of programs described

previously.[4] Further work on polymorph 2 and all computational work on the other polymorphs were carried out on a Syntex XTL structure determination system.[6] The analytical scattering factors of Cromer and Waber were used;[7a] real and imaginary components of anomalous scattering were included in the calculations for all nonhydrogen atoms.[7b]

Polymorph 1. The initial Ni, two P and two S atom positions were determined from a three-dimensional Patterson synthesis. A trial structure factor calculation based on the derived coordinates of these five atoms and a Wilson plot scale factor gave R = 0.433. All of the remaining nonhydrogen atoms except for one nitrile nitrogen atom were located from subsequent difference Fourier syntheses and structure factor calculations. Initially, only the positional parameters were refined; the isotropic temperature factors of the Ni, P's, and the isothiocyanate atoms were then allowed to vary. The bond lengths and angles involving the second isothiocyanate chain (N(2), C(2), S(2)) were unreasonable, and their coordinates were therefore fixed at their initial positions to ensure relative linearity. Table II lists the positional and isotropic temperature factors for all atoms located.

Owing to (a) the high mosaicity ($\omega \sim 3°$) of even the best of all available crystals, and (b) the considerable disorder present in the structure, our analysis was of rather limited success. However, while the bond lengths and angles are of extremely low precision, we feel that the stereochemistry and packing of the molecules has been firmly

established. Further, these latter features of the crystal structure compare favorably with features present in the crystal structures of polymorphs 2 and 3 (see Discussion).

Polymorph 2. In the initial data collection, 3449 reflections were collected, 1965 with $F^2 > 3\ \sigma(F)^2$. The structure was solved with considerable difficulty from a complicated pseudosymmetrical, three-dimensional Patterson synthesis. The complexes occupy the two independent centers of symmetry (0,0,0) and (1/2,0,1/2), which leads to a face-centered arrangement. The face-centered pseudosymmetry was strengthened by the accidental near-coincidence of the Ni-P vectors in the two independent complexes. After the 2Ni, 2P, and 2S atoms were located correctly, the positions of the remaining non-hydrogen atoms were determined from subsequent structure factor and difference Fourier calculations. Least squares refinement with isotropic temperature factors for these atoms led to R = 0.118. A geometry calculation and difference Fourier synthesis revealed considerable disorder in one of the cyanoethyl chains (C(18), C(19), C(20), N(8)). An extensive recollection of the data was undertaken with the hope of improving the overall refinement of the disordered structure (Table I). The final parameters of the initial study were used to commence further refinement. With all nonhyrogen atoms refined anisotropically, and fixed (r_{C-H} = 0.95 Å) calculated H atom positions, R = 0.068, R_w = 0.092 at convergence. However, the molecular geometry of C(18) - C(19) - C(20) - N(8) was unreasonable. Hence, the positions of the latter atoms were

fixed at values corresponding to difference-map coordinates, with isotropic temperature factors. Least-squares refinement under these constraints led to $R = 0.070$, $R_w = 0.107$. Table I reports the final residual density distributions based upon this refinement. A weighting scheme analysis showed no systematic dependence of $w[|F_o| - |F_c|]^2$ on $|F_o|$, $(\sin \theta)/\lambda$, parity of indices, or sequence number. Table III lists the positional and isotropic temperature factors for all atoms, while anisotropic temperature factors appear in Table IV.

Polymorph 3. The positional parameters for the Ni, S, and P atoms were located from a three-dimensional Patterson synthesis. The complex occupies a single crystallographic center of symmetry. A subsequent structure factor calculation and difference Fourier map yielded the positions of the remaining nonhydrogen atoms. After refinement with anisotropic temperature factors for all atoms, a difference Fourier map revealed all the hydrogen atom positions. At convergence, a weighting scheme analysis (vide supra) revealed no systematic dependences. Table V lists the positional and isotropic temperature factors for all atoms, while Table VI lists the anisotropic temperature factors.

Description of the Structures

Figure 1 shows the "pseudo-octahedral" configuration of polymorph 1. This "pseudo-octahedral" configuration is achieved by two distinct features: an intramolecular nitrile N atom nonbonded contact, and, trans to it, an intermolecular S atom nonbonded contact.

Figures 2 and 3, molecular structures of polymorphs 2 and 3, respectively, show the relationship between polymorph 1 and the other two forms. Polymorph 2 is "pseudo-octahedral" by virtue of only intramolecular nonbonded nitrile N-Ni contacts. (The two independent square planar complexes of polymorph 2 have similar configurations to other $NiX_2(CEP)_2$ monomers.)[3] Polymorph 3 is "pseudo-octahedral" by virtue of only intermolecular nonbonded S atom contacts (P - Ni - S' = 96.5°; N(1) - Ni - S' = 75.7°). Hence, the packing of polymorph 1 is a "combination" of polymorphs 2 and 3.

Polymorph 1. Owing to the poor quality of the crystals and the extensive disorder, we here emphasize only the stereochemistry and packing of this species. The intramolecular nonbonded Ni-N (nitrile) distance (3.1 Å) and the nonbonded intermolecular Ni-S distance (3.6 Å) are similar to those found in the other polymorphs (vide infra); the Ni-P bond lengths (2.3 Å and 2.2 Å) and the Ni-N (isothiocyanate) bond lengths (2.1 Å and 2.0 Å) are reasonable. Bond lengths and angles of the ordered atoms are listed in Table VII.

Polymorph 2. Figure 2 depicts the two independent, centrosymmetric square planar complexes, showing the relatively short[8] (3.17 - 3.18 Å) nonbonded Ni-N contacts. While the overall geometry of the phosphine ligand is normal for CEP complexes,[4,9,10] the configuration of the phosphine ligand is different in each complex. However, one cyanoethyl chain in each case has a similar conformation,

which produces the short Ni-N contact. This interaction persists throughout NiX_2CEP_2 structural chemistry in a variety of structures, and it is strikingly absent in $PdCl_2CEP_2$.[11] Pertinent bond lengths and angles are listed in Table VIII. The Ni-N-C angles of 171.21(72)° and 174.88(77)° are within normal limits for square planar Ni(II) complexes.[12,13] The Ni-P (2.214(2) and 2.217(3) Å) distances and the nonbonded Ni-N (nitrile) distances are shorter than those found in other square planar NiX_2CEP_2 complexes.[11,14]

X	Ni-P	Ni-N (nitrile)
Cl	2.239(1) Å	3.31
	2.234(1)	3.26
Br	2.250(1)	3.35
I	2.264(3)	3.41

This is not unexpected in view of the lessened steric requirements around the Ni centers in the present case.

Polymorph 3. The phosphine ligand geometry and the Ni-N-C angle of 171.32(27)° are within experimentally observed ranges. The Ni-P (2.239(1) Å) distance is longer (0.022(3) Å) than in polymorph 2, which may be due to greater steric requirements around the Ni center. The two short, symmetry-related, intermolecular nonbonded S atom contact distances are 3.48 Å (sum of van der Waals radii = 3.40 Å[8]) and the Ni-S′-C′ angle is 151.8°. Other bond lengths and angles are listed in Table IX.

Discussion

Dependence of Polymorphism on Solvent. The choice of solvent for preparation plays a crucial role in both the particular polymorph obtained, as well as the amounts of other forms which arise. Mixing or grinding of $Ni(NCS)_2$ and CEP, without any solvent, invariably yields polymorph 1. Use of an acetone-ethanol mixture again results in predominantly polymorph 1. Crystals of the other polymorphic forms will form on the resultant flocculent precipitate (polymorph 1) but these crystals account for less than 5% of the mas Use of acetonitrile results only in polymorph 1, while crystallization from diacetone alcohol yields only polymorph 3. It is probable that polymorph 1 is at least the kinetically favored crystalline form because of its preferential formation in most organic solvents as well as in the absence of solvents.

The formation of polymorph 3 in diacetone alcohol may be due to slight, but preferential solubility differences. A diacetone alcohol chelated nickel complex has been independently isolated;[4] however, none of the β-hydroxy ketone complex $\{Ni(\text{diacetone alcohol})_2\}\{Ni(NCS)_4(CEP)_2\}$, was obtained when diacetone alcohol was added to the reaction mixtures.

Solid-State Reactivity of the Polymorphs. Visual observations and DSC studies showed no indication of polymerization, as observed in the chloride and bromide analogues, even at elevated temperatures.

However, a reversible solid-state transformation was observed in polymorph 3, at 78°C. Figure 4 shows the reaction proceeding with a distinct front in the [011] direction, the "chain" direction (*vide infra*), accompanied by an apparent increase in crystal volume. The new yellow-orange form is polycrystalline, and its powder pattern (Table X) is indicative of a low symmetry crystal system. Upon cooling below 78°C, the crystal reverts to polymorph 3 (Figure 4b), and the crystal or remaining fragment regains the original external morphology. After approximately eight weeks, the crystal or fragment recovers mostof the original "single crystal" diffraction properties presumably due to a slow "annealing" process. It is not possible to accelerate the "annealing" process by heating.

Crystal Structures. Neither elevated temperature nor pressure effected the interconversion of the three room temperature stable polymorphs. The crystal structure of polymorph 2 (Fig. 5) shows the isolated molecules loosely associated *via* van der Waals interaction. The crystal structures of polymorphs 1 and 3 show an interesting feature (Fig. 6). In polymorph 1 the complexes related by the 2_1 screw axis form a helical arrangement by virtue of Ni-S interactions. The two helices which run through the unit cells are not "crosslinked." However, in polymorph 3, which also consists of helices, the complexes *are* crosslinked *via* Ni-S interactions. It is likely that the lack of strong interactions between the helices in polymorph 1 contributes to the low crystallinity of this complex. It is also

possible that the slow "annealing" process, which occurs in the reversibly-transformed polymorph 3 samples, is a reestablishment of the crosslinkages broken during the phase transformation.

If one envisions a graph of configurational energies versus all possible pathways for generating packing arrangements, only certain pathways leading to, presumably, energy minima, would yield the experimentally found structures. The existence of the three room temperature forms can thus be viewed as a closed set in terms of a "packing coordinate." Two polymorphs have distinct bonding and packing environments while polymorph 1 possesses features common to both.

The conformational polymorphism observed in this work is by no means unique and exists, for example, in substituted n-benzylidene-aniline systems.[15] In order to determine the relationship between crystal structure and molecular conformation, one must determine, in addition to the crystal structures themselves, (1) an estimate of the energy differences in the conformations, (2) lattice energies of the structures, and (3) "partitioning" of the total lattice energy into individual atomic contributions. Even though such computational work has yet to be done, we believe that some of the trends reported by Bernstein and Hagler[15] would be observed in this system: (1) Because the atomic environments in all three forms are not drastically different, the relative contributions of the partial atomic energy to the total energy will be approximately the same; and (2) no single

atom will make an anomalously large contribution to the stabilization of a particular polymorph. However, based on the ease of formation of polymorphs 1 and 3, and the apparent difficulty in obtaining polymorph 2, we believe the role of the nonbonded contacts will be important. Needless to say, it is the sum total of these contributions that ultimately determines the relative stabilities of the polymorphs.

The role of CEP in promoting polymorphic transitions and polymorph formation appears to be crucial. The low steric requirements of this ligand as well as its constrained (linear C-C-N) polyfunctional quality permit various conformations, thus promoting polymorph formation.

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Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (Tables XI-XIII) (n pages). Ordering information is given on any current masthead page.

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Table I

Data for the X-ray Diffraction Study of $Ni(NCS)_2[P(CH_2CH_2CN)_3]_2$

(A) Crystal Data	Polymorph 1	Polymorph 2	Polymorph 3
crystal system:	monoclinic	monoclinic	monoclinic
space group:	$P2_1/c[C_{2h}^5$, No. 14]	$P2_1/c[C_{2h}^5$, No. 14]	$P2_1/c[C_{2h}^5$, No. 14]
a =	13.44(2) Å	16.153(5) Å	11.032(3) Å
b =	9.04(1) Å	12.393(4) Å	10.335(3) Å
c =	24.45(2) Å	13.852(4) Å	11.801(4) Å
β =	115.4 (1) Å	107.89 (4)°	107.21 (5)°
V =	2683 $Å^3$	2638.9 $Å^3$	1285.3 $Å^3$
Z =	4	4	2
Crystal size, mm:	0.38 x 0.04 x 0.04	0.25 x 0.25 x 0.17	0.21 x 0.21 x 0.17
formula wt =	561.3	561.3	561.3
ρ(calcd) =	1.39 g cm^{-3}	1.41 g cm^{-3}	1.450 g cm^{-3}
ρ(obsd)[a] =	1.37 g cm^{-3}	--	1.44 g cm^{-3}
μ (Cu Kα) =	37.0 cm^{-1}	37.6 cm^{-1}	10.6 cm^{-1} [b]
cell constant determination:	9(hkl) and refined 2θ, ω, χ values 8<2θ<25° (λ(CuKα̅) 1.5418Å)	12 pairs ± (hkl) and refined 2θ, ω, χ values, 70 < |2θ| < 90° (λ(CuKα̅) 1.5418 Å)	12 pairs ± (hkl) and refined 2θ, ω, χ values, 27 < |2θ| < 42° (λ(MoKα̅) 0.7107 Å)
(B) Measurement of Intensity Data			
radiation:	CuKα, Ni β filter	CuKα, Ni β filter	MoKα, graphite monochromator

Table I (cont'd)

	Polymorph 1	Polymorph 2	Polymorph 3
reflections measd:	$\pm h$, $\pm k$, $+\ell$ (to $2\theta = 75^{\circ}$)	$+h$, $+k$, $\pm\ell$ (to $2\theta = 123^{\circ}$)	$\pm h$, $+k$, $-\ell$ (to $2\theta = 50^{\circ}$)
scan type, speed:	θ-2θ, fixed, 1.95°/min	θ-2θ, variable, 1.95-6.51°/min	θ-2θ, variable, 1.95-6.51°/min
scan range:	symmetrical $[2.4 + \Delta(\alpha_2 - \alpha_1)]^{\circ}$	symmetrical $[1.6 + \Delta(\alpha_2 - \alpha_1)]^{\circ}$	symmetrical $[2.4 + \Delta(\alpha_2 - \alpha_1)]^{\circ}$
background measurement:	stationary, for one-quarter of scan time at each of scan limits		
no. of reflections measd:	1839 total 1381 in unique set	4326 total 3630 unique	2734 total 2272 unique
standard reflections:	$0\bar{2}0$, 006	$11\bar{3}$, $33\bar{7}$, $46\bar{2}$, 800	$\bar{4}00$, $\bar{4}53$, 123^{c}
automatic recentering after	---	1000 reflections	650 reflections
Absorption correction:	---	empirical	empirical

(C) Treatment of Intensity Data[d]

data reduction: intensities as before,[4] esd's of $|F_o|$ values calcd by method of finite differences, after Churchill et al.[e]

statistical information:	$R_s = 0.062$ $R_{av} = 0.083$	$R_s = 0.027$ $R_{av} = 0.020$ (mainly 0kℓ)	$R_s = 0.020$ $R_{av} = 0.022$ (mainly hk0)

Table I (cont'd)

	Polymorph 1	Polymorph 2	Polymorph 3
(D) Refinement[f]			
no. of data with $F > 3.92\,\sigma(F)$:	519	2499	1852
weighting of reflections:	p = 0.035	p = 0.040	p = 0.030
nonhydrogen atoms (isotropic)	$R = 0.205$[g] $R_w = 0.224$	$R = 0.091$[h] $R_w = 0.127$	$R = 0.108$ $R_w = 0.136$
non-H atoms (anisotropic)	---	$R = 0.070$[i]	$R = 0.038$
H atoms (isotropic)	---	$R_w = 0.107$	$R_w = 0.045$
structure factor calc.	---	$R = 0.103$[i]	$R = 0.052$
all unique data	---	$R_w = 0.111$	$R_w = 0.047$
standard deviation of an obsvn of unit weight	---	2.0310	1.1515
final difference Fourier map:	---	six peaks, 1 $e/\text{Å}^3$ - 0.50 $e/\text{Å}^3$ near atoms of the disordered chain; random peaks ≤ 0.49 $e/\text{Å}^3$	0.52 $e/\text{Å}^3$ near Ni; six other peaks ~ 0.33 $e/\text{Å}^3$ near heavy atoms; random peaks ≤ 0.28 $e/\text{Å}^3$

[a] Measured by flotation in CCl_4-C_6H_{14}

[b] μ (MoKα)

Table I (cont'd)

[c] Linear corrections were applied to data to correct for intensity decay (~ 5%)

[d] $R_s = \Sigma\sigma(|F_o|)/\Sigma|F_o|$; $R_{av} = [(\Sigma||I - I_{av}||)/\Sigma|I|]$ R_s based on $(I > 1.96\sigma(I))$.

[e] Churchill, M.R.; Lashewycz, R. A.; Rotella, F. J. Inorg. Chem. 1977, 16, 265.

[f] $R = \Sigma(|F_o| - |Fc|)/\Sigma|F_o|$

$R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$

$w = [\sigma^2(|F_o|) + (p|F_o|)^2]^{-1}$

$SDU = \{\Sigma w(|F_o| - |F_c|)^2/(m-n)\}^{1/2}$

m (=2499) (Polymorph 2); (=1852) (Polymorph 3) is the number of observations and

n (= 265) (Polymorph 2); (=199) (Polymorph 3) is the number of parameters.

[g] All nonhydrogen atoms except 1 nitrogen atom which was not found.

[h] The Ni and S atoms are anisotropic.

[i] The disordered chain and all hydrogen atoms are isotropic and fixed.

Table II

Atomic Coordinates and Isotropic Temperature Factors for Polymorph 1

ATOM	X	Y	Z	UISO
BI	0.2425	0.3012	0.3520	0.0615
S(1)	0.0282	-0.1062	0.2589	0.0389
S(2)	0.4240	0.7039	0.4580	0.0507
P(1)	0.1639	0.2969	0.4190	0.0602
P(2)	0.3955	0.3021	0.2838	0.0570
N(1)	0.1407	0.1239	0.3092	0.1047
N(2)	0.3248	0.4674	0.4068	0.0810
N(3)	0.0602	0.8649	0.4334	0.0810
N(4)	0.3876	0.0406	0.4193	0.0810
N(5)	-0.1936	0.0924	0.3982	0.0810
N(6)	0.3014	0.8512	0.2282	0.0810
N(7)	0.6315	0.3996	0.4308	0.0810
C(1)	0.0961	0.0315	0.2819	0.0398
C(2)	0.3900	0.5528	0.4288	0.0810
C(3)	0.1532	0.5021	0.4408	0.0923
C(4)	0.0730	0.5732	0.3813	0.0923
C(5)	0.0762	0.7439	0.4072	0.0923
C(6)	0.2796	0.2464	0.5071	0.0923
C(7)	0.3331	0.0569	0.5128	0.0923
C(8)	0.3497	0.0493	0.4564	0.0923
C(9)	0.0462	0.2323	0.3974	0.0923
C(10)	0.0076	0.2107	0.4505	0.0923
C(11)	-0.0734	0.1739	0.4444	0.0923
C(12)	0.3619	0.4879	0.2792	0.0923
C(13)	0.2241	0.5782	0.2436	0.0923
C(14)	0.2754	0.7514	0.2346	0.0923
C(15)	0.4057	0.2188	0.2947	0.0923
C(16)	0.4953	0.2385	0.2995	0.0923
C(17)	0.5437	0.2653	0.3614	0.0923
C(18)	0.1912	0.2252	0.2106	0.0923
C(19)	0.2675	0.2030	0.1632	0.0923
C(20)	0.1539	0.0803	0.0943	0.0923

Table III

Atomic Coordinates and Isotropic Temperature Factors for Polymorph 2 [a]

ATOM	X	Y	Z	UISO
NI(1)	0.0000	0.0000	0.0000	0.0419(9)
NI(2)	0.5000	0.0000	0.5000	0.0545(11)
S(1)	0.10506(18)	-0.02727(26)	0.34651(18)	0.0783(16)
S(2)	0.70569(16)	0.23035(22)	0.69941(18)	0.0667(14)
P(1)	-0.10428(14)	0.10340(18)	0.02263(16)	0.0466(11)
P(2)	0.39707(16)	0.10938(22)	0.51778(20)	0.0638(15)
N(1)	0.05288(43)	-0.00818(58)	0.13618(50)	0.0509(40)
N(2)	0.58576(48)	0.08519(63)	0.58180(54)	0.0587(42)
N(3)	-0.14348(63)	0.03519(78)	0.37595(70)	0.0833(58)
N(4)	0.11050(92)	0.1924(11)	-0.0486(11)	0.146(11)
N(5)	-0.43119(63)	0.04774(96)	-0.16660(77)	0.0967(67)
N(6)	0.47458(77)	-0.16920(98)	0.66107(75)	0.0985(72)
N(7)	0.36465(71)	0.44144(87)	0.41089(80)	0.0950(68)
C(1)	0.07603(52)	-0.01639(72)	0.22374(69)	0.0505(47)
C(2)	0.63613(57)	0.14558(75)	0.63029(62)	0.0509(47)
C(3)	-0.10938(56)	0.11789(73)	0.15201(63)	0.0527(47)
C(4)	-0.13913(59)	0.01376(80)	0.19112(64)	0.0582(50)
C(5)	-0.14129(58)	0.02641(80)	0.29560(73)	0.0598(54)
C(6)	-0.09488(57)	0.23979(71)	-0.01844(70)	0.0592(51)
C(7)	-0.00353(62)	0.28694(80)	0.02034(73)	0.0664(56)
C(8)	0.06005(89)	0.23466(96)	-0.0213(11)	0.0958(82)
C(9)	-0.21222(56)	0.05893(74)	-0.05449(65)	0.0551(48)
C(10)	-0.29061(58)	0.12935(83)	-0.05040(68)	0.0625(53)
C(11)	-0.37051(65)	0.08488(92)	-0.11611(74)	0.0651(57)
C(12)	0.32743(78)	0.0407(11)	0.5762(11)	0.0984(84)
C(13)	0.36825(80)	-0.0181(13)	0.66920(89)	0.1061(90)
C(14)	0.42613(78)	-0.1047(12)	0.66389(80)	0.0770(72)
C(15)	0.43235(61)	0.23349(82)	0.58915(70)	0.0660(57)
C(16)	0.47459(63)	0.31639(84)	0.53919(77)	0.0669(56)
C(17)	0.41317(70)	0.38802(92)	0.46603(86)	0.0718(67)

Table III (cont'd)

N(9)	0.1940	0.2741	0.2005	0.3121
C(10)	0.3239	0.1495	0.3874	0.1241
C(19)	0.2554	0.1969	0.3959	0.1991
C(20)	0.2189	0.2393	0.2738	0.2946
H(3A)	-0.1492	0.1739	0.1531	0.0759
H(3B)	-0.0532	0.1364	0.1954	0.0759
H(4A)	-0.0999	-0.0427	0.1891	0.0759
H(4B)	-0.1958	-0.0042	0.1487	0.0759
H(5A)	-0.1327	0.2843	0.0048	0.0759
H(5B)	-0.1135	0.2405	-0.0964	0.0759
H(7A)	-0.0155	0.3796	0.0930	0.0759
H(7B)	-0.0065	0.3613	0.0029	0.0759
H(9A)	-0.2211	-0.0117	-0.0328	0.0759
H(9B)	-0.2123	0.0565	-0.1231	0.0759
H(10A)	-0.2934	0.2806	-0.0719	0.0759
H(10B)	-0.2971	0.1711	0.0172	0.0759
H(13A)	0.2978	-0.0095	0.5292	0.0759
H(13B)	0.3961	0.0921	0.5998	0.0759
H(17A)	0.3233	-0.0479	0.6917	0.0759
H(17B)	0.4007	0.0323	0.7179	0.0759
H(18A)	0.4771	0.2147	0.6515	0.0759
H(18B)	0.3829	0.2650	0.6002	0.0759
H(19A)	0.5013	0.2731	0.5842	0.0759
H(19B)	0.5119	0.3501	0.5949	0.0759

[a] Standard deviations in the least significant digit appear in parentheses in this and subsequent tables. For atoms refined anisotropically, $U_{iso} = U_{eq} = 1/3 \sum_i \sum_j U_{ij} a^*_i a^*_j a_i \cdot a_j$.

Table IV

Anisotropic Temperature Factors ($\AA^2$) for Polymorph 2[a]

ATOM	U11	U22	U33	U12	U13	U23
NI(1)	0.0444(11)	0.0462(12)	0.02563(99)	0.01039(90)	0.01272(81)	0.00178(85)
NI(2)	0.0522(13)	0.0664(15)	0.0412(11)	-0.0230(11)	0.00898(90)	-0.00172(99)
S(1)	0.0740(17)	0.1132(24)	0.0404(13)	-0.0134(16)	0.0067(12)	0.0116(14)
S(2)	0.0576(14)	0.0813(18)	0.0564(14)	-0.0284(14)	0.0104(11)	-0.0062(13)
P(1)	0.0465(13)	0.0515(14)	0.0416(12)	0.0133(11)	0.01320(96)	-0.00131(99)
P(2)	0.0540(15)	0.0567(18)	0.0569(16)	-0.0136(13)	0.0129(12)	0.0071(13)
N(1)	0.0502(41)	0.0563(50)	0.0351(41)	0.0121(37)	0.0114(32)	-0.0012(36)
N(2)	0.0548(45)	0.0687(52)	0.0455(42)	-0.0176(42)	0.0049(36)	-0.0034(39)
N(3)	0.0998(69)	0.0964(70)	0.0459(57)	-0.0213(56)	0.0437(51)	-0.0174(52)
N(4)	0.156(12)	0.115(10)	0.213(15)	-0.0179(88)	0.126(12)	-0.0558(99)
N(5)	0.0621(61)	0.1312(92)	0.0926(72)	-0.0121(63)	0.0175(55)	0.0079(56)
N(6)	0.1147(89)	0.1075(88)	0.0799(67)	0.0069(71)	0.0396(65)	0.0195(62)
N(7)	0.0978(77)	0.0907(77)	0.0924(75)	0.0166(63)	0.0233(62)	0.0137(60)
C(1)	0.0401(45)	0.0625(59)	0.0508(53)	0.0070(43)	0.0167(40)	0.0015(45)
C(2)	0.0509(53)	0.0586(58)	0.0423(47)	-0.0041(46)	0.0130(41)	0.0067(43)
C(3)	0.0534(53)	0.0597(59)	0.0492(50)	0.0175(45)	0.0196(42)	-0.0080(44)
C(4)	0.0569(53)	0.0761(67)	0.0455(48)	-0.0032(49)	0.0213(42)	-0.0143(48)
C(5)	0.0513(55)	0.0779(69)	0.0529(56)	-0.0042(49)	0.0187(44)	-0.0077(50)
C(6)	0.0545(55)	0.0511(57)	0.0650(57)	0.0047(45)	0.0082(45)	0.0019(46)
C(7)	0.0651(62)	0.0559(61)	0.0737(66)	0.0120(51)	0.0148(52)	-0.0064(51)
C(8)	0.0997(91)	0.0663(78)	0.132(11)	-0.0157(71)	0.1495(85)	-0.0317(76)
C(9)	0.0579(57)	0.0574(57)	0.0534(51)	0.0053(45)	0.0156(43)	-0.0032(44)
C(10)	0.0473(53)	0.0798(71)	0.0595(56)	0.0070(50)	0.0161(44)	-0.0062(52)
C(11)	0.0417(54)	0.0937(80)	0.0562(58)	0.0030(54)	0.0113(47)	-0.0018(55)
C(12)	0.0784(90)	0.1016(95)	0.125(11)	-0.0084(72)	0.0449(77)	0.0126(83)
C(13)	0.0755(79)	0.184(15)	0.0580(72)	0.0195(91)	0.0402(63)	0.0261(86)
C(14)	0.0713(75)	0.103(10)	0.0595(65)	-0.0011(73)	0.0326(60)	0.0243(67)
C(15)	0.0525(61)	0.0715(69)	0.0523(61)	0.0030(53)	0.0169(49)	-0.0037(51)
C(16)	0.0597(63)	0.0519(65)	0.0771(76)	-0.0012(51)	0.0154(53)	-0.0042(54)
C(17)	0.0431(71)	0.0761(79)	0.0793(76)	-0.0139(61)	0.0277(60)	-0.0064(64)

[a] The form of the thermal ellipsoid is $\exp[-2\pi^2(a^{*2}U_{11}h^2 + \ldots + 2b^*c^*U_{23}k\ell)]$.

Table V

Atomic Coordinates and Isotropic Temperature Factors for Polymorph 3

ATOM	X	Y	Z	UISO
NI	0.0000	0.0000	0.0000	0.02379(25)
S	-0.040616(89)	0.345961(90)	-0.251788(84)	0.04990(48)
P	0.200322(65)	0.069361(68)	0.073219(66)	0.02355(33)
N(1)	-0.02806(24)	0.12690(25)	-0.11252(24)	0.0350(13)
N(2)	0.44064(37)	-0.27397(35)	-0.09538(42)	0.0763(23)
N(3)	0.57428(32)	-0.06246(41)	0.22326(35)	0.0668(21)
N(4)	0.19009(47)	0.56081(34)	0.00257(43)	0.0875(27)
C(1)	-0.03625(27)	0.21727(30)	-0.17271(28)	0.0315(14)
C(2)	0.29712(28)	-0.01541(29)	-0.00436(29)	0.0299(14)
C(3)	0.30108(32)	-0.16153(31)	0.01636(34)	0.0363(16)
C(4)	0.37871(33)	-0.22606(33)	-0.04644(36)	0.0459(18)
C(5)	0.27747(30)	0.04217(33)	0.23105(29)	0.0342(15)
C(6)	0.41256(35)	0.08296(38)	0.28706(37)	0.0487(19)
C(7)	0.50445(35)	0.00184(39)	0.25118(35)	0.0480(18)
C(8)	0.23037(28)	0.23799(28)	0.04308(30)	0.0295(15)
C(9)	0.15440(33)	0.33845(30)	0.08813(35)	0.0365(16)
C(10)	0.17284(38)	0.46562(33)	0.04195(38)	0.0496(19)
H(2A)	0.2620(33)	0.0020(31)	-0.0900(34)	0.0399(93)
H(2B)	0.3837(38)	0.0219(35)	0.0125(34)	0.053(11)
H(3A)	0.3345(32)	-0.1937(33)	0.1015(32)	0.0393(94)
H(3B)	0.2193(35)	-0.1970(35)	-0.0172(31)	0.045(10)
H(5A)	0.2176(35)	0.0883(35)	0.2718(32)	0.048(10)
H(5B)	0.2588(35)	-0.0449(38)	0.2499(33)	0.049(11)
H(6A)	0.4221(35)	0.1746(40)	0.2698(34)	0.052(11)
H(6B)	0.4300(40)	0.0742(39)	0.3685(39)	0.060(12)
H(8A)	0.2116(28)	0.2394(29)	-0.0432(28)	0.0238(76)
H(8B)	0.3215(32)	0.2543(30)	0.0754(28)	0.0315(82)
H(9A)	0.1818(29)	0.3385(30)	0.1709(30)	0.0262(80)
H(9B)	0.0675(38)	0.3177(36)	0.0622(33)	0.054(11)

Table VI

Anisotropic Temperature Factors ($\AA^2$) for Polymorph 3[a]

ATOM	U11	U22	U33	U12	U13	U23
NI	0.01646(26)	0.02035(26)	0.03310(30)	-0.00171(21)	0.00507(20)	0.00387(22)
S	0.05190(57)	0.04193(50)	0.05014(57)	-0.00092(42)	0.01087(46)	0.02048(42)
P	0.01643(35)	0.02010(35)	0.03278(42)	-0.00065(28)	0.00521(29)	0.00082(30)
N(1)	0.0284(13)	0.0322(13)	0.0401(16)	-0.0056(11)	0.0035(12)	0.0093(12)
N(2)	0.0653(24)	0.0572(21)	0.1233(35)	0.0021(19)	0.0537(25)	-0.0263(24)
N(3)	0.0325(17)	0.0916(27)	0.0734(25)	0.0101(19)	0.0110(17)	0.0317(23)
N(4)	0.1270(40)	0.0282(18)	0.1134(37)	-0.0076(21)	0.0447(31)	0.0082(20)
C(1)	0.0193(14)	0.0354(17)	0.0367(17)	-0.0052(13)	0.0034(13)	0.0012(15)
C(2)	0.0225(15)	0.0304(16)	0.0383(18)	-0.0030(13)	0.0112(13)	-0.0028(14)
C(3)	0.0310(17)	0.0281(16)	0.0509(22)	0.0006(14)	0.0138(16)	-0.0044(15)
C(4)	0.0332(18)	0.0353(18)	0.0697(26)	-0.0017(15)	0.0160(18)	-0.0099(18)
C(5)	0.0285(17)	0.0376(17)	0.0342(17)	0.0022(14)	0.0056(14)	0.0008(14)
C(6)	0.0377(20)	0.0458(21)	0.0471(23)	-0.0073(17)	-0.0114(17)	-0.0017(19)
C(7)	0.0260(17)	0.0598(24)	0.0490(20)	-0.0066(18)	-0.0034(15)	0.0177(19)
C(8)	0.0213(15)	0.0223(14)	0.0436(20)	-0.0025(12)	0.0077(14)	0.0032(13)
C(9)	0.0357(18)	0.0240(15)	0.0478(22)	-0.0010(14)	0.0092(16)	-0.0019(15)
C(10)	0.0554(24)	0.0272(17)	0.0648(25)	0.0000(16)	0.0156(20)	-0.0039(17)

Table VII

Selected Bond Lengths (Å) and Angles (deg) for Polymorph 1

Ni-P(1)	2.30	Ni-P(2)	2.18
Ni-N(1)	2.08	Ni-N(2)	2.00
N(1)-C(1)	1.08	N(2)-C(2)	1.12
C(1)-S(1)	1.50	C(2)-S(2)	1.52
P(1)-C(3)	1.95	P(2)-C(12)	1.86
C(3)-C(4)	1.53	C(12)-C(13)	1.86
C(4)-C(5)	1.66	C(13)-C(14)	1.76
C(5)-N(3)	1.33	C(14)-N(6)	1.00
P(1)-C(9)	1.55	P(2)-C(18)	1.92
C(9)-C(10)	1.60	C(18)-C(19)	1.82
Ni-S(1)'	3.58		
Ni-N(4)	3.05		
P(1)-Ni-P(2)	177.4		
P(1)-Ni-N(1)	86.6		
P(2)-Ni-N(1)	91.6		

Table VIII

Selected Bond Lengths (Å) and Angles (deg) for Polymorph 2

Ni(1)-P(1)	2.214(2)	Ni(2)-P(2)	2.217(3)
Ni(1)-N(1)	1.819(7)	Ni(2)-N(2)	1.831(8)
N(1)-C(1)	1.159(11)	N(2)-C(2)	1.157(12)
C(1)-S(1)	1.625(9)	C(2)-S(2)	1.619(9)
P(1)-C(3)	1.828(9)	P(2)-C(12)	1.790(14)
C(3)-C(4)	1.533(13)	C(12)-C(13)	1.450(19)
C(5)-C(6)	1.467(13)	C(13)-C(14)	1.441(21)
C(6)-N(3)	1.130(13)	C(14)-N(6)	1.127(19)
P(1)-C(6)	1.805(9)	P(2)-C(15)	1.823(10)
C(6)-C(7)	1.523(14)	C(15)-C(16)	1.513(14)
C(7)-C(8)	1.473(18)	C(16)-C(17)	1.477(15)
C(8)-N(4)	1.128(21)	C(17)-N(7)	1.126(16)
P(1)-C(9)	1.828(9)	P(2)-C(18)	1.895(3)
C(9)-C(10)	1.553(14)	C(18)-C(19)	1.259
C(10)-C(11)	1.441(14)	C(19)-C(20)	1.564
C(11)-N(5)	1.114(15)	C(20)-N(8)	1.062

P(1)-Ni(1)-N(1)	91.19(23)	P(2)-Ni(2)-N(2)	91.68(25)
N(1)-C(1)-S(1)	178.01(84)	N(2)-C(2)-S(2)	179.06(86)
C(5)-C(6)-N(3)	179.28(107)	C(13)-C(14)-N(6)	176.74(141)
C(7)-C(8)-N(4)	176.59(151)	C(16)-C(17)-N(7)	178.25(124)
C(10)-C(11)-N(5)	178.04(119)	C(19)-C(20)-N(8)	174.66

Table IX

Selected Bond Lengths (Å) and Angles (deg) for Polymorph 3

Ni-P	2.239(1)	P-Ni-N(1)	89.21(9)
Ni-N(1)	1.826(3)	N(1)-C(1)-S(1)	176.94(30)
N(1)-C(1)	1.161(4)	C(3)-C(4)-N(2)	178.53(43)
C(1)-S(1)	1.617(3)	C(6)-C(7)-N(3)	178.95(44)
P-C(2)	1.823(3)	C(9)-C(10)-N(4)	176.47(46)
C(2)-C(3)	1.528(4)		
C(3)-C(4)	1.450(5)		
C(4)-N(2)	1.131(6)		
P-C(5)	1.819(3)		
C(5)-C(6)	1.539(5)		
C(6)-C(7)	1.471(6)		
C(7)-N(3)	1.137(6)		
P-C(8)	1.829(3)		
C(8)-C(9)	1.525(5)		
C(9)-C(10)	1.460(5)		
C(10)-N(4)	1.128(5)		
C-H methylene	0.968(11)[a]		

[a]Weighted average

Table X

Interplanar d-Spacings for the High Temperature Form

Number	d(Å)	Intensity
1	3.907	100
2	3.514	95
3	2.831	20
4	2.383	10
5	2.304	70
6	2.173	20
7	2.090	30
8	1.988	80
9	1.846	30
10	1.786	40
11	1.735	20
12	1.641	40
13	1.545	20
14	1.515	20
15	1.444	30
16	1.381	--
17	1.318	--
18	1.255	--
19	1.187	--

Figure 1. Molecular structure of polymorph 1 showing inter-and intramolecular nonbonded contacts to Ni.

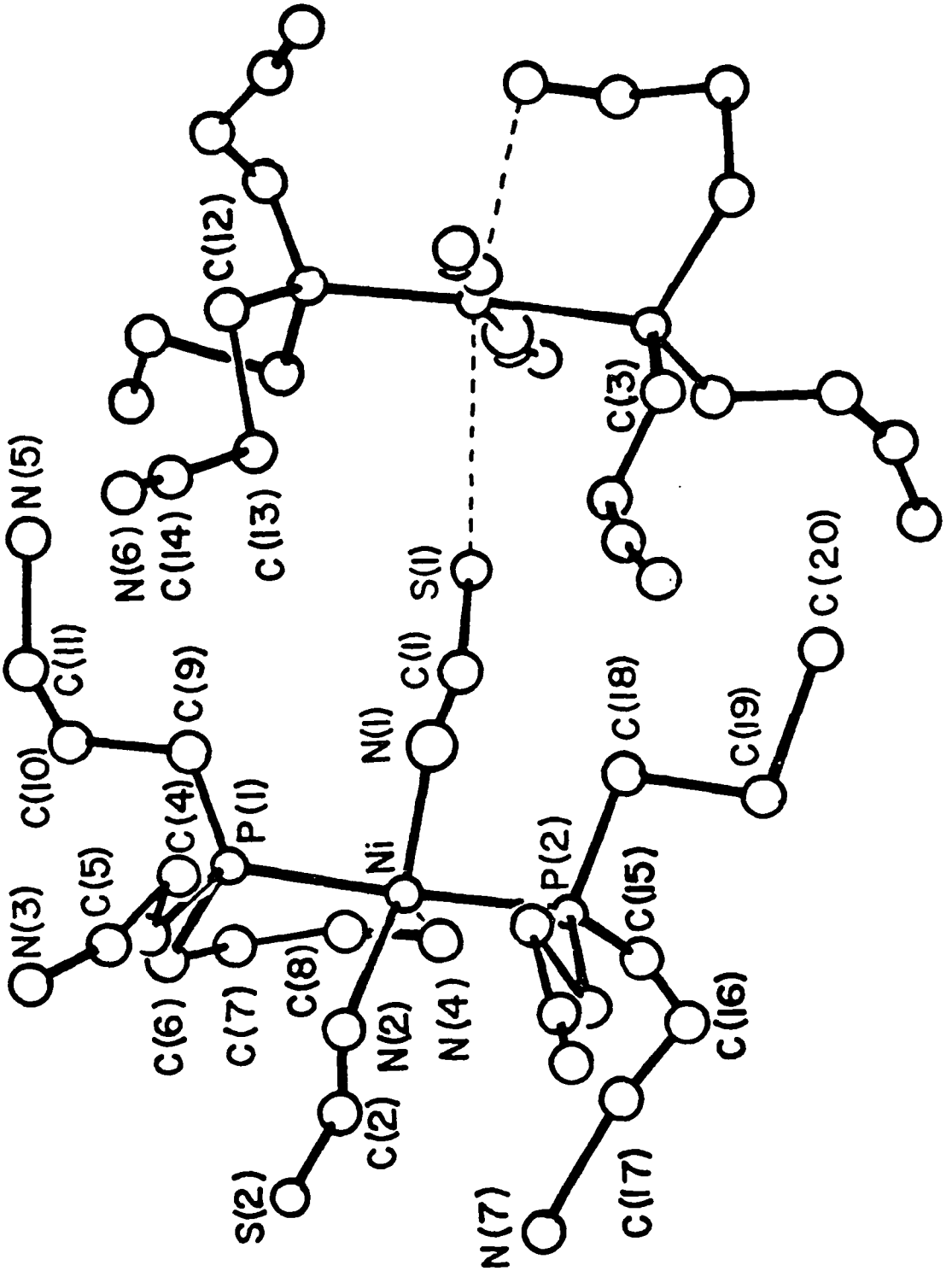
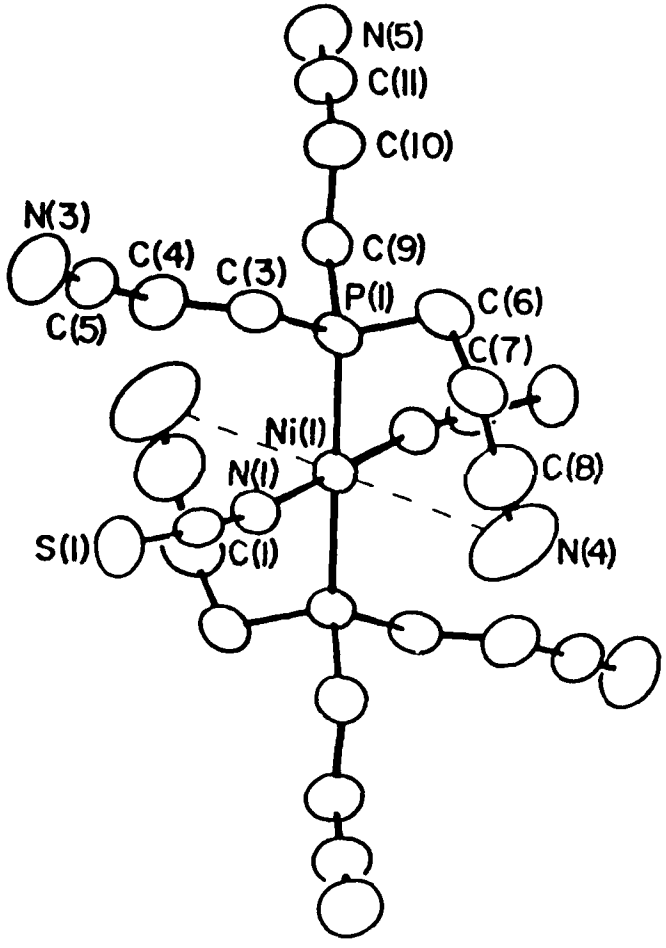

N(5)
C(11)
C(10)
N(3)
C(5)
C(4)
C(9)
P(1)
C(6)
C(7)
C(8)
Ni
N(1)
C(1)
S(1)
N(2)
N(4)
C(2)
S(2)
N(6)
C(14)
C(12)
C(13)
P(2)
C(18)
C(19)
C(20)
C(15)
C(16)
C(17)
N(7)
C(3)

Figure 2. Molecular structures of (from left) the non-disordered and the disordered polymorph 2 complexes with 50% probability ellipsoids for atoms refined anisotropically.


N(5)
C(11)
C(10)
N(3)
C(4)
C(3)
C(9)
C(5)
P(1)
C(6)
C(7)
Ni(1)
N(1)
C(8)
S(1)
C(1)
N(4)

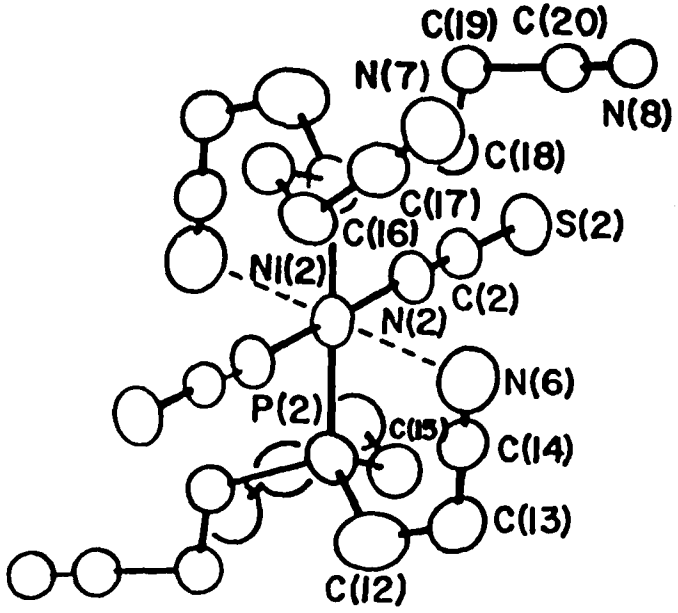

C(19)
C(20)
N(7)
N(8)
C(18)
C(17)
C(16)
S(2)
Ni(2)
C(2)
N(2)
N(6)
P(2)
C(15)
C(14)
C(13)
C(12)

Figure 3. Molecular structure of polymorph 3 showing intermolecular non-bonded contacts from two neighboring molecules.

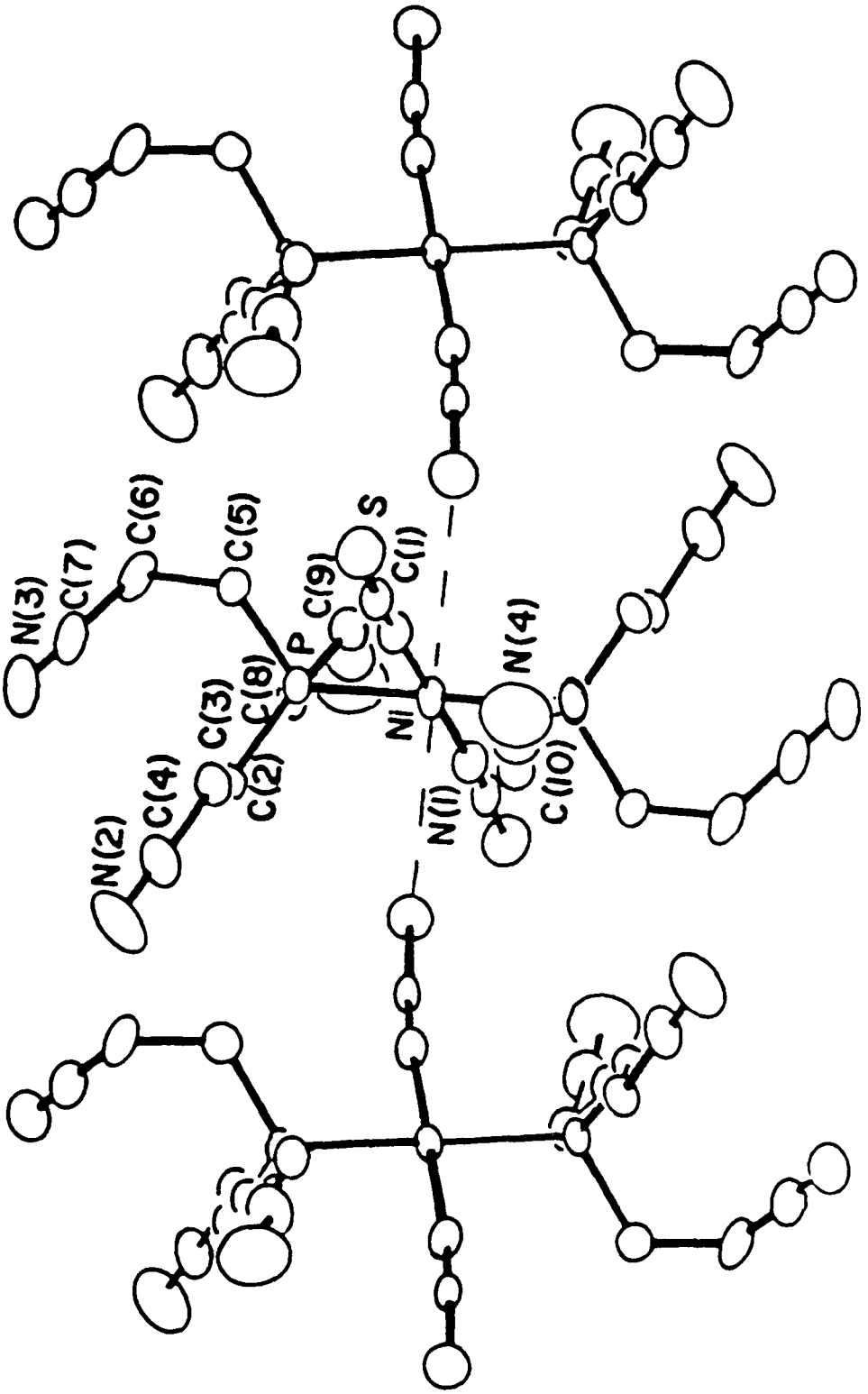

N(3)
C(7)
C(6)
C(5)
S
C(1)
C(9)
P
C(8)
C(3)
C(2)
C(4)
N(2)
Ni
N(4)
N(1)
C(10)

Figure 4. (a) Polymorph 3 reacting to form the high temperature form. The crystal is being heated to the transition temperature (78°C) on the hot stage of a Fisher Model 355 Digital Melting Point Analyzer. The second photograph shows the front moving across the crystal, as well as a change in crystal shape.

(b) Demonstration of the reversibility of the reaction; some fragmentation of the crystal occurs, but the original habit is partially regenerated upon cooling (final photograph). The steel pin used as a heat source here is not touching the crystal in the second photograph but rather obscures the view. Occasionally, fragmentation does not occur, and, upon cooling, the original habit is completely regenerated.

4a:

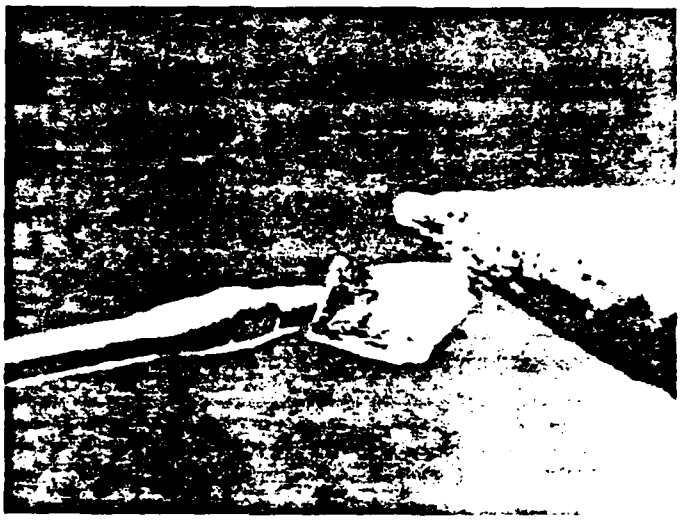
(1)

(2)

46.

(1)

(2)



(3)

Figure 5. The crystal structure of polymorph 2. The dahsed lines indicate nonbonded intramolecular Ni-N(nitrile) contacts.

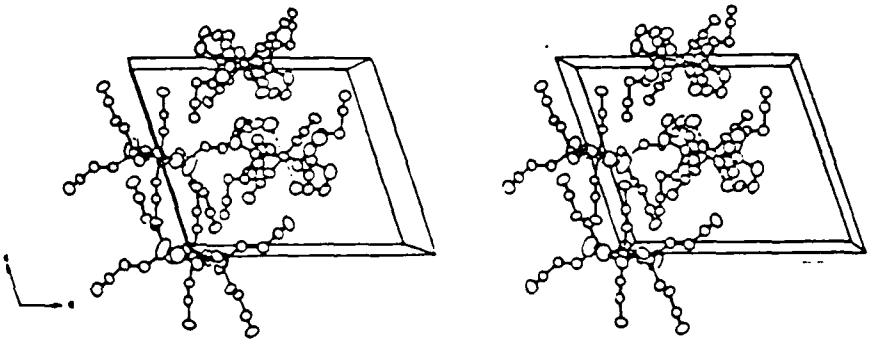
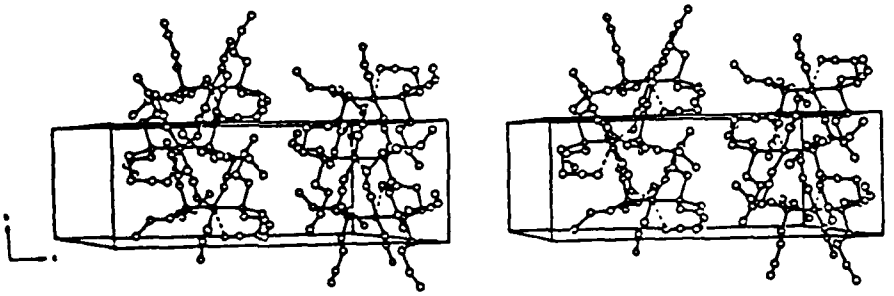
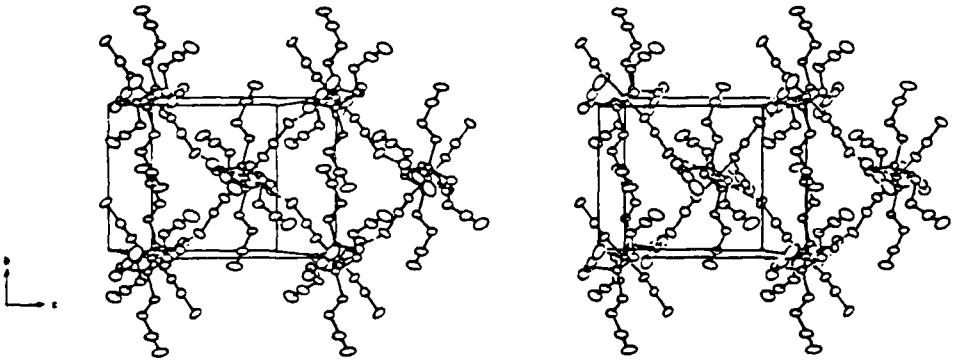


Figure 6. (a) The crystal structure of polymorph 1 depicting the helical arrangements and the nonbonded Ni-S and Ni-N (nitrile) contacts (dashed lines). (b) The crystal structure of polymorph 3 depicting the "crosslinked" helical arrangements and the nonbonded Ni-S contacts (dashed lines).





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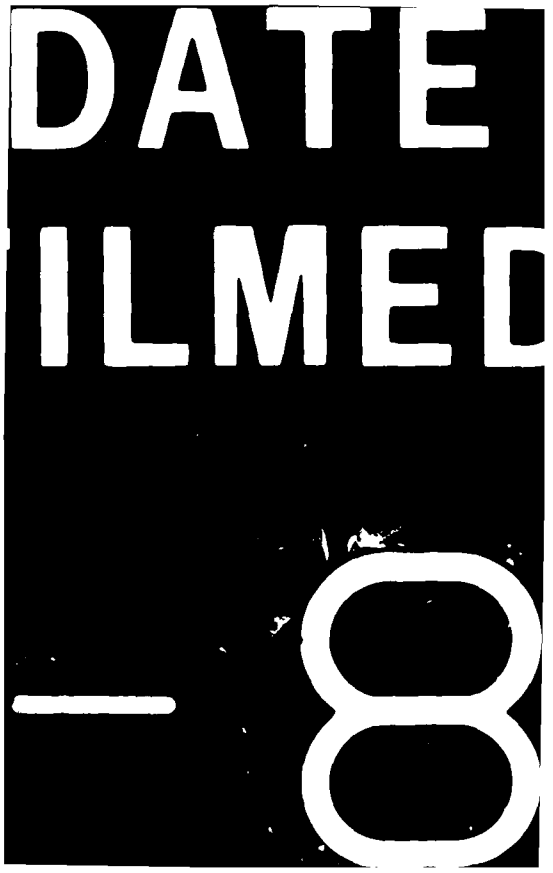
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